

# **Laser Sensor Development for Fluorescence Detection of Plastics and other Anthropogenic Compounds Dissolved in Seawater**

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## **LONG TERM GOALS**

The long-term goal is to build and deploy a highly sensitive, *in situ* AUV-mounted instrument designed to locate and identify plastic and rubber-coated objects, such as mines, in the water column and buried within the seafloor. It is anticipated that a compact, single laser LIF system with optical filtered PMT detectors will provide real time detection of plastic and carbon compounds. Projected limits of sensitivity *in situ* are in the range of parts per trillion (ppt) for this sensor, an improvement of orders of magnitude over existing fluorescence sensors. Oceanographic applications include UV-vis spectral characterization of dissolved and particulate (phytoplankton) fluorescence for remote sensing, plume tracking, and pollution applications. The multi-channel UV laser-induced fluorescence sensor (MUVLIFS) will ultimately be integrated and deployed on an autonomous underwater vehicle (AUV) to enhance strategic and oceanographic applications.

## **OBJECTIVES**

The short term goals are to test a compact UV laser multi-channel fluorometer system for shipboard use in enhanced measurement of UV-stimulated fluorescent compounds in seawater, and to develop algorithms enabling discrimination between naturally-occurring and anthropogenic compounds. Consideration must be given to the seawater fluorescence caused by natural organic matter, which will comprise most of the background signal. We also propose to develop and construct an UV laser multi-channel fluorometer that can be used *in situ* to detect and monitor artificial and natural organic substances in seawater.

## **APPROACH**

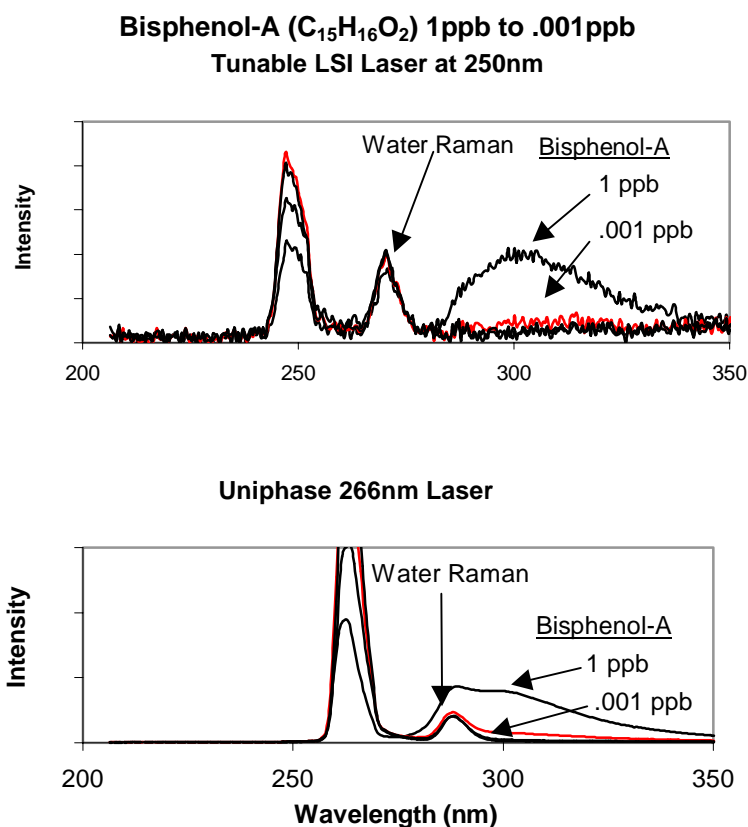
During this funding year the laser induced fluorescence (LIF) system has been improved and miniaturized, and laboratory measurements have continued. We have started the initial phase for the construction of a portable LIF system for shipboard use.

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## WORK COMPLETED

Previously, chemical proxies for fluorescence of leachates were determined from deformation and chemical analyses of commercial marine epoxy systems (Chemir/Polytech, Inc.). Results of the chemical analyses indicate that the water leachates contain components derived from epoxy systems based on bisphenol A. By comparing the fluorescence fingerprints of mine leachates with those of the pure components we were able to match bisphenol A itself with the characteristic UV peaks found in the mine leachates. Sensitivity tests with smaller laser/optical setups have been performed with bisphenol A and quinine sulfate, a well-characterized fluorescence standard.

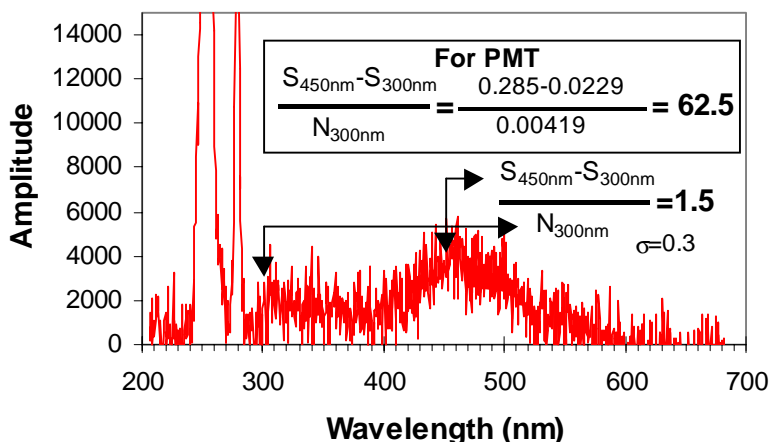
Experiments continued to determine the effects of photodegradation on fluorescence from both seawater background and the chemical proxies. Samples were irradiated using an optical parametric oscillator (OPO) pumped with the third harmonic output of a Nd:YAG laser (355 nm) pulsed at 10 Hz. Waters collected from the Tampa Bay estuary provided river and marine influenced endmembers for fluorescence analysis. Results provide useful insight into the composition of the original DOM. Based on observed spectral properties, high-energy monochromatic light destroyed several distinct, possibly pure, compounds that exhibited dual excitation peaks. Ubiquity of dual excitation peaks in photo-destroyed compounds indicates that most UV-C fluorophores of CDOM also generate UV-B fluorescence. This is postulated to be a universal feature of CDOM fluorescence, with source-specific variability in exact peak positions for CDOM from different environments.



### *1. LIF Spectra from Bisphenol-A Using the Tunable LSI Laser at 250nm and the Fixed Wavelength Uniphase 266nm Laser.*

The sensor prototype LIF system has been upgraded, and the original laser/detector system and new, smaller LIF components can be run simultaneously for calibration and comparison. The current frequency-doubled nitrogen pumped dye laser provides variable UV wavelengths from 240nm to 275nm at up to .03mW (3μJ 10Hz PRF) for general laboratory spectral studies. A new (4x) Nd:YAG microchip laser operating at a fixed wavelength of 266nm and 1.5mW (.2μJ 7.5kHz PRF) has been added to the system, which will be used in the shipboard and AUV systems. The increase in average power of the microchip laser improves signal to noise without the sample bleaching problems seen with past high-powered lasers. This solid state microchip laser will be used in the portable system for on ship use and eventually in the AUV system. Figure 1 shows comparative spectra from bisphenol A using the fixed wavelength 266nm Uniphase laser and the tunable LSI laser at 250nm. The fixed wavelength Uniphase laser (average power of 1.5mW) has a better signal to noise than the LSI tunable laser (average power .03mW) and better sensitivity down to about .001 ppb of bisphenol A. However, the spectral separation and detection of bisphenol A fluorescence from the water Raman peak for the LSI system is better due to its 250nm excitation wavelength.

Improvements have also been made to the detection system. The original detection system consisted of a 15cm Spectrometer with a 300 lines/mm grating and a TE cooled UV Si 1024x128 pixel CCD camera. A simpler and more compact light collection system consisting of 5 optical bandpass filters, a PMT, and a boxcar integrator has been constructed. Gated PMT's usually have better signal to noise than CCD's. The addition of a boxcar integrator improves signal to noise in a pulsed system by taking measurements for a short time around the pulse and excluding times when there is only noise. Figure 2

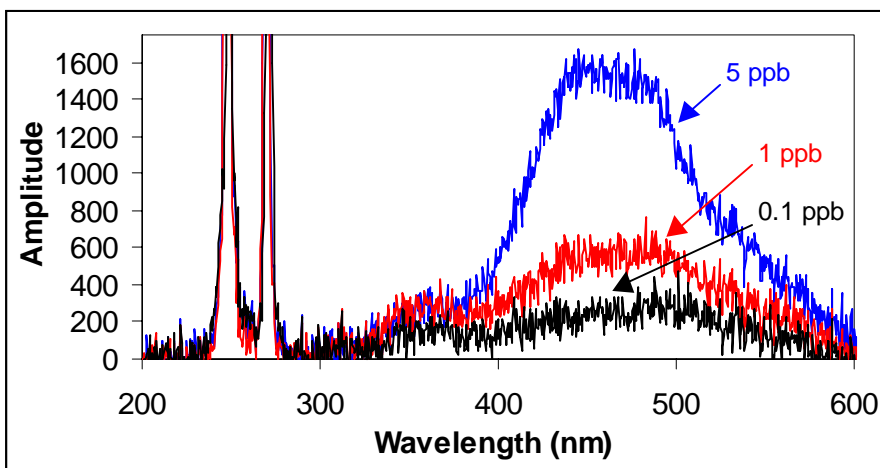


## 2. LIF spectra of QS using original spectrometer/CCD and 250nm excitation.

Detection	S/N
Spectrometer/CCD	1.5
Spectrometer/PMT	5
Filters/PMT	62

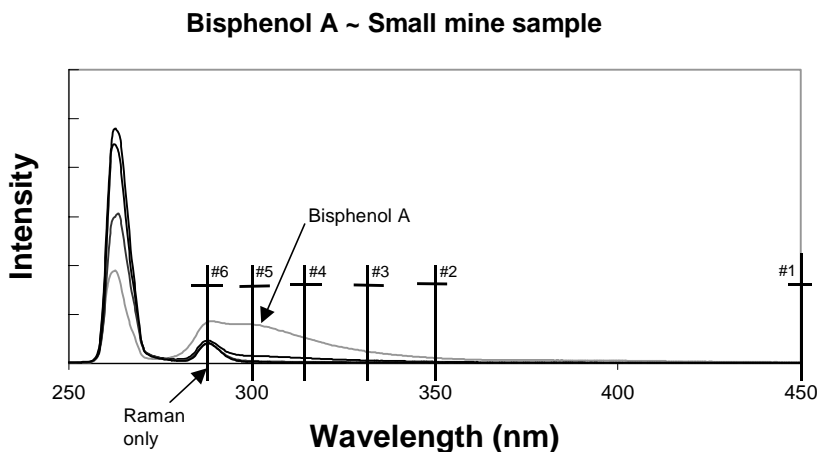
Table 1. Comparison of Measured S/N Values  
LSI Laser @ 250nm; 1ppb QS

shows an example of the data used to calculate the signal to noise for the original spectrometer/CCD system and Table 1 show the results for the various detector systems we have tested. The signal to noise is calculated by taking the difference between the signals at 450nm and 300nm and then dividing by the noise at 300nm. The signal to noise for the original spectrometer/CCD system was 1.5.



### 3. LIF spectra of QS as a function of concentration using spectrometer/CCD and 250nm excitation

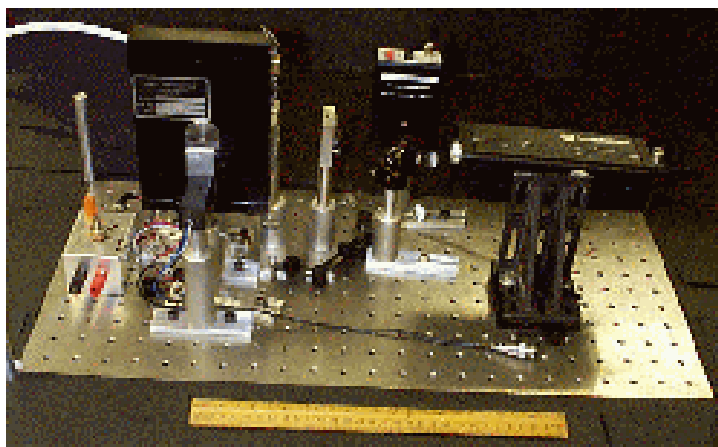
The signal to noise for the PMT system was measured to be 62 i.e.  $(S_{450nm} - S_{300nm})/N_{300nm} = (0.285 - 0.0229)/0.00419 = 62$ . The optical band filters / PMT system has 40 times better signal to noise than the original spectrometer / CCD system and is estimated to have 12 times better signal to noise than a system using the spectrometer with a PMT in place of the CCD. Figure 3 shows data collected with the CCD with 3μJ pulses down to 0.1 ppb QS, which is close to the detection limits of that system.



### 4. LIF signal from Bisphenol A at concentrations of 1 ppb to 1 pptr using fixed wavelength 266 nm laser. Also shown is the approximate placement of optical bandpass filters to be used in the multi-wavelength PMT AUV LIF system.

Of importance for the fixed excitation laser/PMT detector system is the placement of the optical filter band centers. Figure 4 shows the center wavelength of six optical band pass filters chosen to detect the Raman signal near 290 nm, the mine plastic signal between 300 to 335 nm, and dissolved organic matter near 450 nm. Five filters can be included in the filter wheel and PMT detector system at one time, depending on the wavelengths of interest. Work to lower the background to improve sensitivity is continuing.

We have started the initial phase for the construction of a portable shipboard LIF system use utilizing 1-inch optics (shown in Fig. 5). The mobile setup will utilize a 110 Volt AC electrical source available on board ship, and fits on a 12x24x1inch optical table in a watertight case. The case will remain closed during operation to shield the system from outside light. Based on results of preliminary



*5. Portable LIF system.*

field design, the AUV system is expected to be powered by a combination of 12-volt DC batteries. A power budget is currently being conducted, but early estimates are on the order of a few hundred watts. The LIF system is predicted to fit into a 2' x 2' x 3' container, and weigh about 50 pounds.

## **RELATED PROJECTS**

The MUVLIFS unit is targeted for multisensor applications to increase the level of certainty that a mine does or does not exist. We will test the performance of both shipboard and AUV systems in local waters in conjunction with an ongoing study jointly funded by the ONR-HYCODE Program and the EPA/NOAA EcoHAB Program. In addition to optimization for mine detection, we will assess sensor performance for oceanographic applications. The data from laboratory studies on effects of environmental factors on mine leachate behavior in seawater will be combined with field data on fluorescence fingerprints and intensity of seawater background, DOC concentration, hydrography, and measurements of circulation on the West Florida shelf to revise our mine detection feasibility scenario.

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